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(21) International Application Number: PCT/AU85/00113 (22) International Filing Date: 27 May 1985 (27.05.85) (71) Applicant (for all designated States except US): THE UNIVERSITY OF MELBOURNE [AU/AU]; Park- ville, VIC (AU). (72) Inventor; and (75) Inventor/Applicant (for US only) : MARTIN, William, Reginald, Bulmer [AU/AU]; 48 Cuthbert Street, Cor- nellia, VIC 3948 (AU). (74) Agent: SANDERCOCK, SMITH & BEADLE; 203 Riversdale Road, Hawthorn, VIC 3122 (AU). (81) Designated States: DE, GB, JP, US.		Published <i>With international search report.</i>
(54) Title: METAL HALIDE REDUCTION WITH MOLTEN SODIUM/POTASSIUM ALLOY (57) Abstract A method of obtaining a desired metal, selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten, which comprises reacting a halide of the desired metal with an alkali metal reducing agent at a temperature at which the reducing agent is molten, in order to produce the desired metal and halide of the metal reducing agent.		

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METAL HALIDE REDUCTION WITH MOLTEN SODIUM/POTASSIUM ALLOY

This invention relates to chemical processes. In another aspect this invention relates to chemical processes involving reactive metal(s) in the liquid state at temperatures and pressures such that the other reactants, generally covalent halides, are present in compact phase, i.e. not in the gaseous phase.

I have found that in chemical processes wherein one of the reactants is a suitable metal or is a suitable metal mixture, in the liquid state, substantial and unexpected advantages accrue from employment of the liquid metal in considerable stoichiometric excess. Inter alia, the invention takes advantage of the extraordinarily high capability to transfer heat which is exhibited by metals in the liquid state. The excess liquid metal also functions as a materials transfer agent.

The present invention provides a method of obtaining a desired metal selected from the group consisting of metals capable of existing in the form of a compound capable of being reduced with a liquid metal reducing agent which comprises a reaction comprising contacting such a compound of said desired metal in substantially compact form with a liquid metal reducing agent whereby to obtain said desired metal.

Preferably said compound is a covalent halide.

Preferably said desired metal is selected from the group consisting of titanium, aluminium, iron, manganese, hafnium, zirconium, tantalum, vanadium, uranium and tungsten.

In a particularly preferred aspect the present invention provides a method of obtaining a desired metal selected from the group consisting of titanium, aluminium, iron, manganese hafnium, zirconium, tantalum, vanadium, uranium and tungsten which comprises a reaction comprising contacting a halide of said desired metal in substantially compact form with a liquid metal reducing agent whereby to obtain said desired metal.

Particular advantage is derived from application of the

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1 invention to recovery of titanium from its tetrachloride
2 which is directly derivable from ores such as rutile.

3 High purity titanium metal is today a strategic
4 material, for example in space research and for high speed
5 aircraft. It is expensive to produce by conventional means;
6 firstly because it is so reactive at high temperatures,
7 especially temperatures greater than 500°C and, it is
8 particularly reactive with respect to oxygen.

9 A development of the invention envisages the
10 preparation of alloys which are required to be free to
11 impurities, particularly oxygen, such as iron titanium and
12 titanium iron manganese alloys. Alloys such as these can be
13 used to store hydrogen in the form of hydrides and the
14 amount of hydrogen which can be stored is inversely
15 dependant on the amount of oxygen contamination.

16 The alloys referred to above as hydrogen stores may
17 provide a satisfactory source of hydrogen for use as a fuel
18 for internal combustion engines and for storage of energy
19 via the fully reversible heat of reaction.

20 Oxygen is ubiquitously present in air and water and
21 only a few parts per million are required to adversely
22 affect the properties of high purity titanium metal and the
23 types of alloys mentioned herein. Consequently very special
24 techniques are needed to produce titanium metal in oxygen-
25 free condition.

26 It is recognized that "commercial pure" titanium
27 capitalises upon the presence of impurity oxygen which is
28 controlled, like carbon in steel, to increase the stiffness
29 in ambient temperature conditions for corrosion resistant
30 duty as in chemical plants.

31 Because of the special nature of the covalent titanium
32 halide compounds, particularly the chlorides, it is possible
33 to purify them entirely from oxygen reasonably easily and in
34 a continuous plant. However, existing processes for recovery
35 of titanium metal from the halide invariably result in
36 surface contamination from air and/or water arising from
37 recovery of the "sponge" from solidified melts. Only
38 coarsely crystalline material with low surface/volume ratio

1 can be used for high purity metal. Fine titanium adsorbs so
2 much water and/or air on its surface that subsequent melting
3 under argon at minimum pressure to maintain an electric arc
4 yields a metal ingot unacceptably high in oxygen for high
5 purity metal. Furthermore, fine titanium powder is generally
6 pyrophoric and must be handled in an inert atmosphere.

7 The invention is also applicable to the obtaining of
8 other metals as noted above and of these another
9 particularly economically significant metal is aluminium.
10 However, care needs to be applied in obtaining an anhydrous
11 halide and it is desirable that the halide be in liquid
12 phase.

13 Many halides may be put in liquid phase, if that is not
14 their normal condition, by heat and/or pressure so as to
15 liquefy them but it is also possible to dissolve halides in
16 inert solvents such as a paraffin or suspend it in a liquid
17 or even use reactive solvents such as ferri chloride and
18 titanium tetrachloride..

19 However, experimental work does show that even if the
20 halide is in solid form reaction does occur.

21 Preferably said liquid metal reducing agent comprises a
22 metal selected from the group consisting of Group I metals
23 or a mixture containing a Group I metal.

24 Preferably said liquid metal reducing agent is a
25 mixture of sodium and potassium alloy.

26 Said liquid metal reducing agent may contain at least
27 one of calcium and magnesium.

28 It is desirable that said reaction is conducted at a
29 temperature not greater than the boiling point or
30 sublimation point of the halide under the pressure
31 pertaining.

32 It is desirable that said reaction is conducted at a
33 temperature such that solid by-product halides of said
34 liquid metal reducing agent are formed.

35 The reaction is greatly exothermic. When using NaK
36 alloy in the presence of approximately equivalent amounts of
37 reactants without cooling, the evoked heat caused the
38 reaction to "run away" with a resultant explosion. This is

1 avoided, in accordance with the present invention, by
2 employment of the liquid metal reducing agent in
3 considerable excess to transfer the heat to an external
4 sink. The excess liquid metal reducing agent not only
5 displaces the equilibrium in favour of the reaction; while
6 part of the liquid metal reducing agent reacts and ceases to
7 be metallic, the excess continues to act as a potent
8 reductant but also acts as a highly efficient heat transfer
9 medium, in situ, at the actual reactive zone where the heat
10 is produced. A high yield of fully reduced desired metal is
11 obtained by operating under these conditions, at a suitable
12 reactor temperature. Partially this is because the strongly
13 electro positive liquid metal reducing agent not only acts
14 as a carrier and heat transfer medium but also as an
15 unrestricted source of electrons by electronic conduction,
16 once the covalent bonds of the halide of the desired metal
17 are split. Substantially full reduction to desired metal
18 occurs. There was no evidence that lesser reduction to
19 undesired metal cations occurs. Working with excess liquid
20 metal reducing agent in intimate contact with a compact
21 phase in contrast to a disperse vapour, is an important
22 advance over prior art processes which at low temperatures
23 have produced desired metal in low yields, due to partial
24 reduction to lower halides.

25 If desired, heat might be removed from the reaction by
26 circulating the liquid metal reducing agent to a cooling
27 station but in general the conductivity of the liquid metal
28 reducing agent will be effective in carrying heat to the
29 wall of a reaction vessel from which heat may be removed.

30 In one instance at least portion of said liquid metal
31 reducing agent is circulated between the reaction vessel and
32 reaction product removal station whereby to convey reaction
33 products away from said reaction vessel.

34 Preferably said liquid metal reducing agent is present
35 in stoichiometric excess.

36 Preferably said desired metal that is produced is
37 removed from said reaction with the liquid metal reducing
38 agent and is thereafter separated from by-product halides of

1 said liquid metal reducing agent and from the liquid metal
2 reducing agent.

3 The operating pressure of the process should preferably
4 be maintained by rare gas, e.g. argon, the current economic
5 choice.

6 The process according to the invention may be carried
7 out continuously and in such case excess liquid metal may be
8 employed as a carrier to remove the reaction products at low
9 temperature from the reaction vessel to suitable filters,
10 screens, decantation vessels and/or centrifuges or vacuum
11 distillation stages. A liquid slurry of the liquid metal
12 reducing agent and reaction products will flow and can be
13 pumped by known means.

14 The product salts (sodium chloride and/or potassium
15 chloride) may be separated from the much heavier desired
16 metal powder in a centrifuge, and the excess sodium,
17 potassium or NaK alloy may then be centrifuged or filtered
18 from these separately. Finally the residual NaK metal may be
19 evaporated under high vacuum from the titanium powder after
20 particle modification if desired, in a higher temperature
21 loop.

22 In general, complete removal of liquid metal reducing
23 agent halides from liquid metal reducing agent which is to
24 be reused is not considered essential as such halides
25 probably act as seeds for reaction initiation.

26 Anhydrous ammonia will be found useful in removing
27 traces of liquid metal reducing agent from desired metal.

28 Preferably said reaction is initiated by liquefying
29 said halide and, if necessary, a precursor material in solid
30 form of said liquid metal reducing agent.

31 It is possible to pass liquid sodium metal
32 countercurrent to by-product halides of said liquid metal
33 reducing agent whereby to regenerate potassium metal from
34 potassium chloride.

35 For high purity compact product metal, powder produced
36 by the process of the present invention is preferably
37 directly melted by the electron beam technique, which avoids
38 the contamination experienced in the use of electric arcs on

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1 water washed metal powder or that which has been exposed to
2 the air. An electric arc must have a minimum amount of gas
3 present to ionise, and will not operate in an ultra high
4 vacuum that would strip all gases off hot surfaces. In
5 conventional arc processes argon or helium atmospheres are
6 employed but the absolute pressure necessary prevents good
7 stripping of air and water vapour from the washed metal
8 powder.

9 Electron beam melting is generally becoming the
10 preferred compacting means in rare and contaminatable metal
11 technology, for example that of titanium, hafnium,
12 zirconium, tantalum and tungsten.

13 Thus in a preferred embodiment of the invention, metal
14 powder from which the residual NaK alloy has been
15 evaporated, is fed directly into the melting electron beam
16 without ever having been exposed to air or water. In these
17 circumstances small particle size is advantageous. Also
18 electroslag melting may be applicable.

19 In another embodiment powder suitably conditioned in a
20 hot loop may be released to ambient and handled
21 conventionally for use in powder metallurgy or for hydrogen
22 storage as hydride. Treatment with an alcohol or ketone has
23 been found to reduce and in some cases eliminate pyrophoric
24 problems.

25 Because liquid sodium reduces potassium from its molten
26 salts (cf vice versa in aqueous media), no difficulty in
27 keeping potassium captive in the system is anticipated. In
28 one proposed embodiment of the invention, for continuous
29 production of titanium, liquid Na metal from an electrolytic
30 reduction cell would enter the process counter current to
31 outgoing mixed product NaCl and KCl stream. This counter
32 current contacting, with sufficient heat and mass transfer
33 stages, would both retain the K in the system and conserve
34 the heat.

35 Then overall the feed to the process would be, $TiCl_4$
36 and Na metal and the products, be Ti metal and NaCl which
37 latter could be recycled directly to an electrolytic cell
38 from which in turn Cl_2 would be available either to an

1 integrated TiCl_4 production plant or for sale according to
2 economics of procurement of TiCl_4 and titanium source
3 materials, e.g. rutile plus carbon, at the plant site. For
4 economic reasons site melted Na brought into the site, may
5 be better than recycle to an integrated electrolytic cell,
6 without affecting the generality of the principle of captive
7 K, which essentially removes its cost from the economics of
8 production, this being essentially tied to TiCl_4 and Na in
9 and $\text{Ti} + \text{NaCl}$ out of the essential process. Similar
10 considerations apply to other desired metals.

11 EXAMPLE 1

12 Titanium metal was recovered from TiCl_4 by reaction
13 with a large excess of NaK alloy.

14 The apparatus incorporated means for evacuating the
15 system to below 10 microns of mercury; a supply of inert
16 gas; the means for external heating and cooling a reactor,
17 with a heat transfer medium inert to NaK. The reactor was
18 made of pyrex glass so that the reaction mixture was clearly
19 visible. A stirrer totally isolated from ambient was built
20 into the reactor, and means for sampling while stirring
21 while under inert gas or vacuum were provided. Safety of
22 operation was a paramount consideration.

23 The stirrer was adjustable and made of nickel tubing,
24 as it is known that nickel is an inert reaction vessel
25 material for the preparation of titanium from its chlorides.
26 As autocatalysis may be important in the mechanism,
27 facilities were provided for both nickel and titanium
28 propellers on the stirrer.

29 The reactor was made of pyrex glass, surrounded by a
30 pyrex glass jacket through which high flash point, low
31 viscosity oil was pumped to either heat or cool the
32 reactants. The jacket, in particular the base, was designed
33 to maintain high heat transfer rates at the vessel walls.
34 Inside the reactor, the stirred liquid NaK alloy itself
35 constituted an excellent heat transfer medium. On one side
36 of the vessel was provided a connection to a burette
37 containing TiCl_4 , and on the other side a vent to a mercury
38 lute. A sampling probe was also provided.

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1 A thermocouple was connected into the cooling system at
2 the point where the oil leaves the glass jacket surrounding
3 the reactor.

4 The lute provided was adapted to vent to atmosphere any
5 pressure surge which may occur in the system, yet allow a
6 high vacuum to be applied to the system.

7 Argon gas was used as the protective gas, as is
8 customary the preparation of titanium, but facilities for
9 using nitrogen were also built into the system. The argon
10 used was a commercially pure grade, and was purified of any
11 traces of water vapour and oxygen before admission following
12 evacuation.

13 The titanium tetrachloride used was laboratory reagent
14 grade, which was distilled in an atmosphere of nitrogen
15 before use, the boiling range 133°C to 136°C being
16 collected.

17 60/40 mole % NaK sodium-potassium alloy was prepared. 30
18 g (1020 millimoles) of the alloy was charged into the
19 reactor via a No. 3 porous filter disc, under the cover of
20 argon gas, and the tetrachloride was placed in a burette
21 which had a fitting to connect it to the reactor.

22 The stirrer was set running and 2.00 ml. (18
23 millimoles) of $TiCl_4$ was added to the alloy. The reaction
24 mixture was stirred vigorously. The top layer of alloy
25 became darker and went through a wide range of colours;
26 gold, blue, pink and green all being noticeable. Then
27 another 1.20 ml (11 millimoles) of $TiCl_4$ was added and once
28 again many colours were visible, then 70 seconds after the
29 addition, there was a flash of light, and a recorder showed
30 a rapid 0.8°C increase in the temperature of cooling fluid
31 from about 25°C. A dark grey substance was now seen inside
32 the apparatus intermixed with the liquid metal. There was
33 evidence of a considerable increase in the viscosity of the
34 excess liquid metal.

35 The whole system was evacuated to remove any remaining
36 $TiCl_4$ (none was found in subsequent tests on the cold trap
37 washings). To facilitate analysis of the products, two lots
38 of 25 ml. of ethanol (436 millimoles each) were added to

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1 destroy the alloy.

2 When all the alloy was destroyed, suction was applied
3 to a sample probe inserted into the reactor and as much
4 material as possible was withdrawn into the filter. The
5 solid's were filtered and washed with ethanol and then dried
6 under vacuum. The reaction vessel also contained a quantity
7 of rather finer solids and these were also collected and
8 washed with ethanol, but kept separate from the coarser
9 samples. The two samples were extracted with hot water, and
10 after drying, the mass of water-insoluble material was 1.53
11 g, 1.12 g from the coarse sample and 0.41 g from the fine
12 sample.

13 Metallurgical examination indicated that both samples
14 after the above treatment comprised non-pyrophoric titanium.

15 For purpose of examination, they were dissolved in hot
16 dilute sulphuric acid, precipitated with ammonia and ignited
17 to TiO_2 . The yield was close to theoretical.

18 EXAMPLE II

19 The procedure of Example I was repeated excepting that
20 $AlCl_3$ was used in lieu of $TiCl_4$.

21 Aluminium metal was produced although yields were low
22 and reaction times long probably due to the fact that the
23 $AlCl_3$ remained in solid state throughout the process; the
24 apparatus used being incapable of holding the pressure
25 necessary to liquefy $AlCl_3$ under the temperatures that were
26 practical.

27 EXAMPLE III

28 While the process exemplified in Example II proved the
29 process of this invention as applicable to aluminium,
30 further experiment was made to improve yields by conducting
31 the process inside a sealed bomb so as to ensure
32 liquefaction of $AlCl_3$.

33 30g of a 60/40 mole % NaK sodium - potassium alloy was
34 charged into a bomb under inert atmosphere conditions and
35 10gm of dry freshly prepared $AlCl_3$ was also charged into the
36 bomb under inert atmosphere conditions.

37 The bomb was sealed and heated to $300^\circ C$ and maintained
38 at that temperature for 15m.

1 After cooling, the bomb was unsealed under an inert
2 atmosphere and the NaK alloy was destroyed and product metal
3 was extracted similarly as in Example I.

4 A yield of aluminium of 80% of theoretical was
5 obtained.

6 This example indicates the desirability of the halide
7 being in liquid phase.

8 By the use of the exemplary processes we can provide a
9 pure metal such as titanium, aluminium or an alloy such as
10 TiFe suitable for the new hydride storage technology or
11 other metals or mixtures of metals for which truly anhydrous
12 halides are preferred.

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1 CLAIMS

- 2 1. A method of obtaining a desired metal selected from the
3 group consisting of metals capable of existing in the form
4 of a compound capable of being reduced with a liquid metal
5 reducing agent which comprises a reaction comprising
6 contacting such a compound of said desired metal in
7 substantially compact form with a liquid metal reducing
8 agent whereby to obtain said desired metal.
- 9 2. A method as claimed in claim 1, wherein said compound
10 is a covalent halide.
- 11 3. A method as claimed in claim 1, wherein said desired
12 metal is selected from the group consisting of titanium,
13 aluminium, iron, manganese, hafnium, zirconium, tantalum,
14 vanadium, uranium and tungsten.
- 15 4. A method of obtaining a desired metal selected from the
16 group consisting of titanium, aluminium, iron, manganese,
17 hafnium, zirconium, tantalum, vanadium, uranium and tungsten
18 which comprises a reaction comprising contacting a halide of
19 said desired metal in substantially compact form with a
20 liquid metal reducing agent whereby to obtain said desired
21 metal.
- 22 5. A method as claimed in claim 4, wherein said desired
23 metal is titanium.
- 24 6. A method as claimed in claim 4, wherein said desired
25 metal is aluminium.
- 26 7. A method as claimed in claim 4, wherein the halide is
27 an anhydrous halide.
- 28 8. A method as claimed in claim 4 wherein the halide is in
29 liquid phase.
- 30 9. A method as claimed in claim 8, wherein the halide is
31 in solution.
- 32 10. A method as claimed in claim 8, wherein the halide is
33 in suspension.
- 34 11. A method as claimed in claim 8, wherein the halide is
35 in liquefied form.
- 36 12. A method as claimed in claim 4, wherein the halide is
37 in solid form.
- 38 13. A method as claimed in any preceding claim wherein


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- 1 said liquid metal reducing agent comprises a metal selected
2 from the group consisting of Group I metals or a mixture
3 containing a Group I metal.
- 4 14. A method as claimed in claim 13, wherein said liquid
5 metal reducing agent is a mixture of sodium and potassium
6 alloy.
- 7 15. A method as claimed in claim 13, wherein said liquid
8 metal reducing agent addition alloy includes at least one of
9 calcium and magnesium.
- 10 16. A method as claimed in any preceding claim wherein
11 said reaction is conducted under substantially anhydrous
12 conditions.
- 13 17. A method as claimed in claim 4, wherein said reaction
14 is conducted at a temperature and pressure such that the
15 halide and said liquid metal reducing agent are maintained
16 in liquefied form.
- 17 18. A method as claimed in claim 17, wherein said reaction
18 is conducted at a temperature not greater than the boiling
19 point or sublimation point of the halide under the pressure
20 pertaining.
- 21 19. A method as claimed in claim 17, wherein said reaction
22 is conducted at a temperature such that solid by-product
23 halides of said liquid metal reducing agent are formed.
- 24 20. A method as claimed in any preceding claim, wherein
25 said reaction is conducted under substantially oxygen free
26 conditions.
- 27 21. A method as claimed in any preceding claim which is
28 conducted in a reaction vessel and wherein at least a
29 portion of said liquid metal reducing agent is circulated
30 between the reaction vessel and a reaction product removal
31 station whereby to convey reaction products away from said
32 reaction vessel.
- 33 22. A method as claimed in any preceding claim, wherein
34 said liquid metal reducing agent is present in
35 stoichiometric excess.
- 36 23. A method as claimed in any preceding claim wherein said
37 reaction is effected under an inert atmosphere.
- 38 24. A method as claimed in claim 4, wherein said desired

- 1 metal that is produced is removed from said reaction with
2 the liquid metal reducing agent and is thereafter separated
3 from by-product halides of said liquid metal reducing agent
4 and from the liquid metal reducing agent.
- 5 25. A method as claimed in any preceding claim wherein said
6 reaction is initiated by liquefying said halide and, if
7 necessary, a precursor material in solid form of said liquid
8 metal reducing agent.
- 9 26. A method as claimed in claim 14, comprising passing
10 liquid sodium metal countercurrent to by-product halides of
11 said liquid metal reducing agent whereby to regenerate
12 potassium metal from potassium chloride.
- 13 27. A method as claimed in any preceding claim, including
14 applying an alcohol or a ketone to the desired metal that is
15 produced prior to exposing it to ambient atmosphere.
- 16 28. A method of producing a metal substantially as
17 hereinbefore described with reference to any one of the
18 Examples.
- 19 29. The articles, things, parts, elements, steps, features,
20 methods, processes, compounds and compositions referred to
21 or indicated in the specification and/or claims of the
22 application individually or collectively, and any and all
23 combinations of any two or more of such.

INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 85/00113

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ⁴ C22B 34/12, 5/04, 21/04		
II. FIELDS SEARCHED Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C22B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
AU : IPC as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	AU,B, 2299/51 (155702) (TITAN COMPANY) 5 July 1951 (05.07.51)	(1-5,7,13,16, 20,21-24)
X	AU,B, 4415/51 (152033) (TITAN COMPANY) 11 October 1951 (11.10.51)	(1-5,7,12,13, 16,19,20,22-24)
X	AU,B, 14243/52 (162433) (ICI) 22 January 1953 (22.01.53)	(1-5,7,8,12,13, 16-18,20,22,23)
X	US,A, 3951647 (CARDWELL et al) 20 April 1976 (20.04.76)	(1-4,8,13,16, 20,22,23)
X	US,A, 4105192 (ISHIMATSU et al) 8 August 1978 (08.08.78)	(1-4,7,8,13, 14,16-18)
X	AU,B, 13626/55 (215185) (PETER SPENCE & SONS) 24 May 1956 (24.05.56)	(1-5,7,8,12,13, 16,17,20,22,23)
X	AU,B, 26334/57 (219663) (SHELTON) 26 September 1957 (26.09.57)	(1-5,7,8,11, 13-18,20-24)
X	AU,B, 25003/54 (166613) (NRDC) 15 April 1954 (15.04.54)	(1-5,7,8,11-24)
X	AU,B, 26401/54 (167668) (NATIONAL LEAD COMPANY) 10 June 1954 (10.06.54)	(1-5,7,8,12,13, 16-24)
X	AU,B, 16391/56 (212759) (UNION CARBIDE AND CARSON CORPORATION) 15 November 1956 (15.11.56)	(1-8,11,13, 16-20,23,24)
¹⁰ Special categories of cited documents: ¹¹ "A" document defining the general state of the art which is not considered to be of particular relevance ¹² "E" earlier document but published on or after the international filing date ¹³ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) ¹⁴ "O" document referring to an oral disclosure, use, exhibition or other means ¹⁵ "P" document published prior to the international filing date but later than the priority date claimed ¹⁶ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention ¹⁷ "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step ¹⁸ "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art ¹⁹ "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 22 November 1985 (22.11.85)		Date of Mailing of this International Search Report 09 DECEMBER 1985 (09.12.85)
International Searching Authority Australian Patent Office		Signature of Authorizing Officer 

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 85/00113

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Members	
US	4105192	FR 2300816	JP 51092711
US	3951647	DE 2252567	JP 48072017

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